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MICROSCOPIC AND MICROCHEMICAL STUDY OF AGED SOLID PROPELLANT GRAINS

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FOREWORD

This technical report was prepared under Contract No. AF 04(611)-11637 as partial fulfillment of the requirements of Project No. 3148 of the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards, California. The work was done in the Advanced Propellants Department, Research and Technology Operations, Aerojet-General Corporation, Sacramento, California. This report was designated Aerojet-General Report 1082-81Q-1 and covers the results of work done during the interval 18 July to 31 October, 1966. This project was monitored by Lt. Robert Bargmeyer.

Acknowledgement is made to the following persons who have contributed materially to the work performed during this period:

At Aerojet-General

J. T. Becerril, Senior Laboratory Technician, B. B. White, Manager, Mechanical Properties Laboratory, H. D. Orcutt, Electron Microscopist, W. Hartmann, Hawk Projects.

At Hill Air Force Base

Mr. Leo Granath

At Thiokol Chemical Corporation

Mr. Paden

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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ABSTRACT

Considerable effort was expended to acquire samples of old propellants to be studied. Propellants from 2 Hawk motors (age, $5\frac{1}{2}$ years) were obtained and progress was made toward getting samples of a Minuteman Wing I, first stage motor. An inventory of samples already on hand indicated a varied assortment of propellants from 3 months to $7\frac{1}{2}$ years in age. Model propellants were cast and cured to compare the effects of accelerated aging with normal aging.

Optical investigation of Hawk and Polaris Cycling Unit propellants reveal that the concentration of reaction sites is greater at the open end. In a Minuteman Ignitor propellant subjected to accelerated aging, the concentration of aging reaction sites is the same at both the closed and the open ends.

Micromanipulation of the aging sites indicated that the polymer had degraded and could be easily separated into phases. It was demonstrated that a De Fonbrune Microforge could be used to prepare a number of micro-utensils for use in this study. An electron diffraction pattern of a non-melting solid in an aging site was obtained but its interpretation was not carried out.

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MICROSCOPIC AND MICROCHEMICAL STUDY OF AGED SOLID PROPELLANT GRAINS

I. INTRODUCTION

This is the first Quarterly Technical Report submitted in partial fulfillment of the requirements of Contract AF 04(611)-11637. The report covers the period 18 July to 31 October 1966.

The objectives of this study are to determine the course of the chemical aging process or processes in solid propellant formulations and to define the effects of these degradative chemical processes on the mechanical and ballistic properties of the propellant.

In accordance with these general objectives, the studies have been divided into two phases. The objectives in Phase I are to determine the structure, size and distribution of microscopic reaction sites in solid propellants as a function of age, formulation and storage environments; and to optically characterize and chemically analyze the reaction intermediates and products. In Phase II the mechanistic course of the aging process will be defined.

Work during the first quarter consisted of acquisition of propellant from field aged motors, preparation of model propellant grains for accelerated aging studies, exploratory microscopic examination of the acquired samples, and initiation of optical and related microscopic studies.

II. PROPELLANT ACQUISITION

A. TYPE AND AGE OF SAMPLES

Previous work showed that microscopic reaction sites[1] occurred in samples of propellant taken from field aged motors formulated from polyurethane, aluminum, ferric acetylacetonate and ammonium perchlorate. Therefore, grains of this type were acquired first and other formulations will be acquired and examined later.

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(1) J. L. McGurk, "Determination of Near Solid State Changes in Aged Propellants", A.I.A.A. Journal, 3, 1890 (1965).

The ages of grains containing reaction sites were between 3 and 7 years. Reaction sites were not observed in field aged grains less than three years of age. Grains over 7.5 years were not examined. The concentration of reaction sites increased with time and their internal structure also changed. Both these characteristics differed between formulations. Thorough comparison of several different formulations from full scale motors of different ages would be ideal, but not practical. Therefore, samples cut from motors during previous years and stored in our laboratory facility will be used. In these samples the reaction apparently stopped when the sample was cut from the grain so that the nominal age at time of cutting will be recorded plus a note as to its true age.

B. MOTOR GEOMETRY AND AGING SITES

Since, in a motor the reaction sites form a concentration gradient in both radial and axial directions and analysis of the entire grain was not feasible, some part of the gradient had to be selected for sampling. Furthermore, the grain area selected for microscopic study might not be the best for chemical analysis; thus considerable exploratory work was necessary prior to the selection of regions in the grain to be studied.

The relationship of the concentration gradient to motor geometry is a significant factor in this study. However, schematic grain diagrams are used to indicate sample location and more accurate diagrams will be prepared when specific gradients are to be shown.

C. PROPELLANTS ACQUIRED

1. Hawk Motors 15062 and 15121

The principal samples acquired during the first quarter were from two 5½ year old Hawk motors.

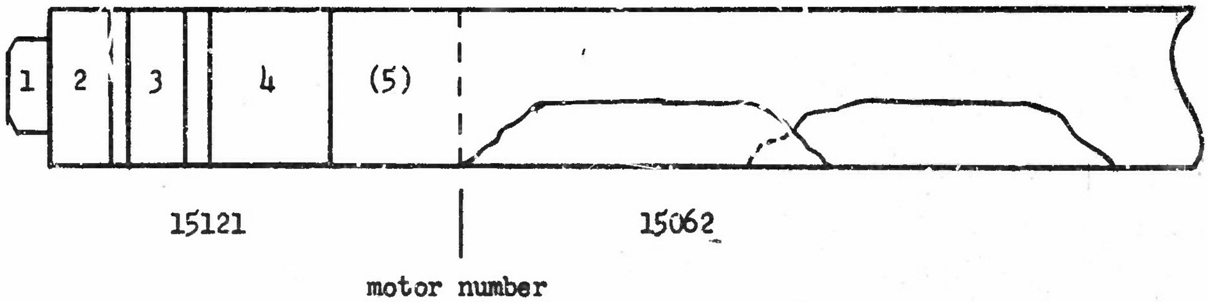
The Hawk, motor 15121, was from an Army surveillance program of field motors. The storage history will be reported later. The aft closure was removed and two cylindrical sections (2 and 3, Figure 1) were machined from the grain by Hawk projects at Aerojet-General. The motor was then transferred to this program. Because of the small bore diameter, additional propellant could not be turned out on the lathe and the steel case was cut at a distance of 23 inches from the aft end by an electrolytic method. The grain was then parted with a saw and a cylinder of propellant 10 inches long (Section 4, Figure 1) was slipped out of the case. Machining causes the loss of several inches of propellant which is not lost when the electrolytic method is used. Another Hawk motor, 15062, from the same surveillance group failed during test firing and samples were recovered and reassembled so that their original geometrical location could be determined. The schematic, Figure 1, of the Hawk shows the approximate sample size and position in both motors.

2. Minuteman First Stage Wing I Propellant

Additional effort consisted of arranging, with the help of Lt. Bargmeyer (EAFB) and Mr. Granath (Hill AFB), for samples from a Minuteman First Stage Wing I motor being sectioned by Thiokol Chemical Corp. In arranging for these samples, a diagram showing suggested sample locations was sent to Mr. Granath. The actual sample locations will be reported when the sample and related data are received.

Figure 1

Schematic Outline of Hawk Grain Indicating Areas from which Propellant was Removed



3. Previously Cut Samples Stored at Aerojet

The most important samples in laboratory storage are those from a Polaris Cycling Unit and consist of ray sections, 10 inches long, from both fore and aft ends. Several of these sections were cut when the grain was 5½ years old in 1964, and one more was cut at 7½ years in 1966.

4. Samples on Hand

The samples now on hand are listed in Table 1 giving the nominal age, weight and formula designation.

Table 1

PROPELLANTS AVAILABLE FOR AGING STUDY

Motor	Age	Weight	ANP
Hawk	5½ years	150 lbs	2832 Mod I 2830 Mod I
Hawk	4½ years	5 lbs	2832 Mod I 2830 Mod I
Cycling Unit	7½ years	10 lbs	2639
Cycling Unit	5½ years	50 lbs	2639
Tartar	2 years	5 lbs	2915 Mod I
Minuteman Ignitor	3 months	2 oz	2758 Mod II
Minuteman Ignitor	9 months	2 oz	2758 Mod II
Minuteman Ignitor	12 months	2 oz	2758 Mod II
Minuteman Ignitor	1 year	2 oz	2758 Mod II

III. PREPARATION OF MODEL GRAINS

Just prior to the start of the program, microscopic aging reaction sites were observed in some Minuteman Ignitor grains undergoing accelerated aging. About the same time a sample of an ignitor grain was obtained from a field aged motor. Comparison of the microscopic reaction sites showed a difference in distribution between the field aged and accelerated aging samples. To study their difference and provide samples from slightly different formulations, some grains were cast using the ignitor formulation. Two motors of 3KS-1000 size were prepared in split Micarta cylinders, 4.75 inches in diameter and 18.6 inches long, with a gear core. These were cut in half providing four grains which were placed in ovens of different temperatures. The intent of this procedure was to gain information on specific reactions that might be temperature dependent. Two motors of the same size were prepared with a bipropellant configuration using the Hawk formulation to investigate its accelerated aging characteristics. The propellant in these motors did not cure and a decision concerning new preparation of these model grains was not made.

The program for storage and sampling of the model ignitor grains is to store three of the grains at 180°F, 122°F and 110°F. The fourth grain will be cycled between 130°F and 50°F. Sampling will be monthly for the next three months and quarterly thereafter. Initial microscopic studies showed that no reaction sites are present.

IV. OPTICAL AND RELATED MICROSCOPIC PROCEDURES

A. EXPLORATORY STUDIES OF MICROTOMED THIN SECTIONS

Optical work consisted of exploratory microscopic studies on propellant thin sections taken from the samples in order to program motor dissection. The aft end of the Hawk grain contained a high concentration of colored reaction sites along the bipropellant interface. The concentration decreased toward the fore end. The samples from the failed motor which were near the center of the motor did not contain the reaction sites. A concentration gradient appeared to exist and this was confirmed by examining the fore and aft end of sample 4 in the Hawk motor shown in Figure 1. When Section 5 is removed, a continuous section between the two motors will be available and conditions along the axial gradient can be studied.

A curious difference in the distribution of reaction sites was observed. In the Cycling Unit which was open on both ends, the end samples had approximately the same concentration of reaction sites. In the Hawk motor which was open on the aft end, the concentration of reaction sites decreased toward the closed forward end. However, the 12 month ignitor motor which was aged at accelerated conditions had the same concentration at both ends, although the motor was sealed at one end only.

B. RELATED MICROSCOPIC PROCEDURES

To investigate the structure and composition of the reaction site, micromanipulators were set up and used to obtain data on structural properties of the reaction site such as the hardness, elasticity and interface adhesion between the different optical phases. Initial attempts were very successful. Probes could be used at maximum objective power and the thin section could easily be held in place with controlled movements of the microscope mechanical stage. With two manipulator probes, the sequence of photomicrographs in Figure 2 was taken. Figure 2b shows separation of the binder from the aluminum when the probes are shifted latterally from the position in Figure 2a. Repositioning of the probes in Figure 2c and then pulling them apart in Figure 2d, causes separation of two or more gel phases in the binder. By repeating the same movements in an area away from the reaction site, the binder phase stretched, but no failure occurred. The ease with which separation of binder phases in the reaction site is evidence that within the reaction site bonds have been broken in the once continuous polymer phase.

C. CHEMICAL MICROSCOPY PREPARATION

A De Fonbrune Microforge was borrowed from Aloe Scientific Co. Micropipettes and microcones shown in Figure 3 were prepared. Figure 3a shows a delivery tip of a pipette with a uniform taper and clean sharp tip. Further up, the shank has a uniform cylindrical section, as shown in Figure 3b. Observation of a liquid miniscus in this area with a grid reticle in the microscope eyepiece will permit delivery of pico and nanoliter volumes of liquids. The reaction vessel is called a cone and is shown in Figure 3c. The small size of the cones made handling difficult and a procedure was developed for welding a stem on to the cone as shown in Figure 3d. This microglassware is used with the micromanipulators. The cones are mounted in a humidity cell on the microscope stage while the micropipette is held in the micromanipulater and connected to a syringe for delivery of solution to the cone. The sample of unknown is delivered to the cone with one of a series of microprobes.

D. ELECTRON MICROSCOPY

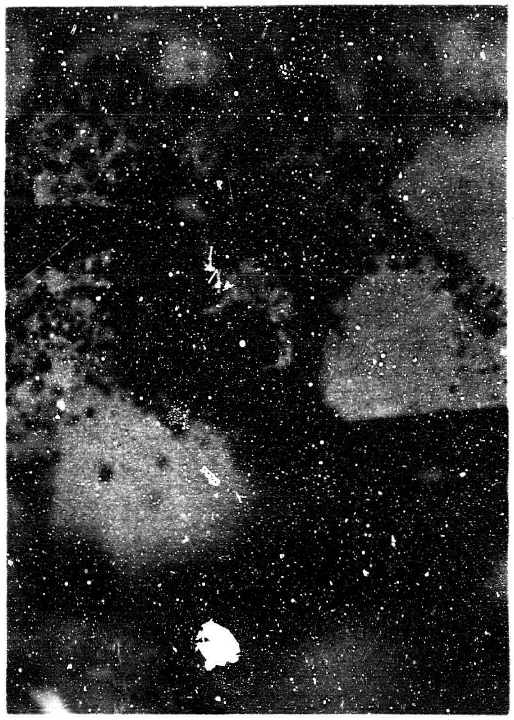
Thin sections of propellant, less than one micron thick, were microtomed with the diamond knife and examined in the transmission beam of the electron microscope. The binder phase tended to slowly burn in the electron beam and the NH_4ClO_4 decomposed while the metal phases remained unchanged. However, these processes were slow enough so that the reaction site features could be examined. Various morphological features could be noted for comparison, characteristic melting difference under a higher beam intensity permitted differentiation of aluminum from other solids (presumed to be copper chromite), and some very good electron diffraction patterns were obtained from these non-melting metals. Interpretation of the diffraction pattern has yet to be carried out. This technique should yield information on the role of Cu and Cr in the previously postulated Fe- and Al-binder reactions.

V. FUTURE WORK

The effort during the next three months will be more in the optical laboratory, chemical studies will be initiated, and there will be less effort on sample acquisition.

MICROMANIPULATION OF REACTION SITES

a



b

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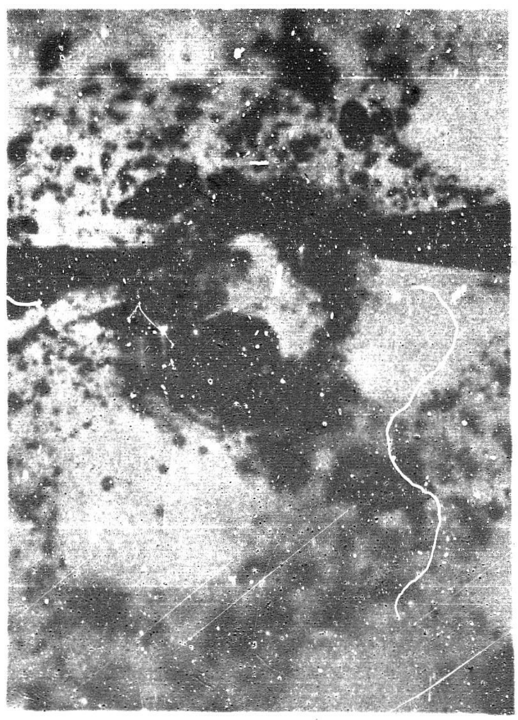
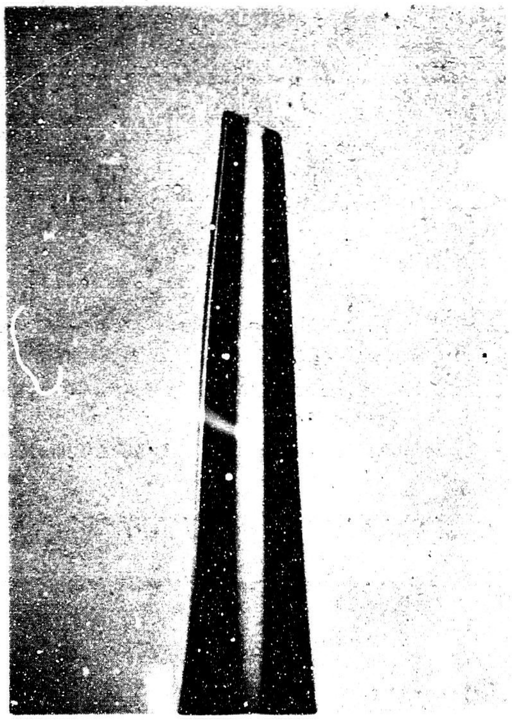


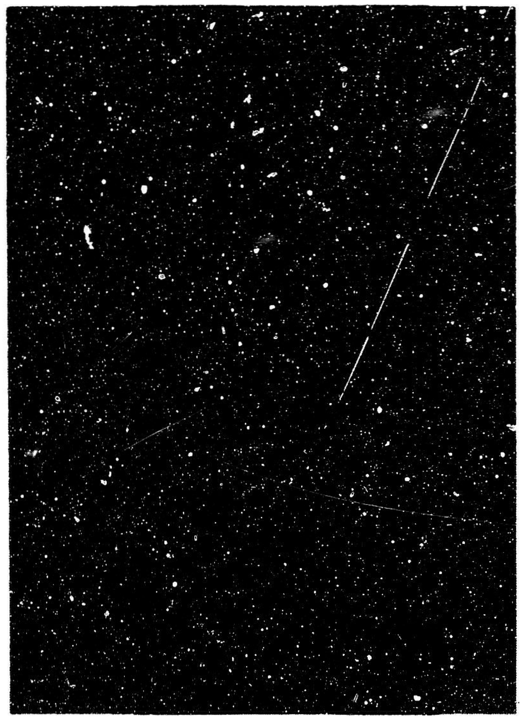
d

Figure 2

MICRO PIPETTES AND CONES



a 100X



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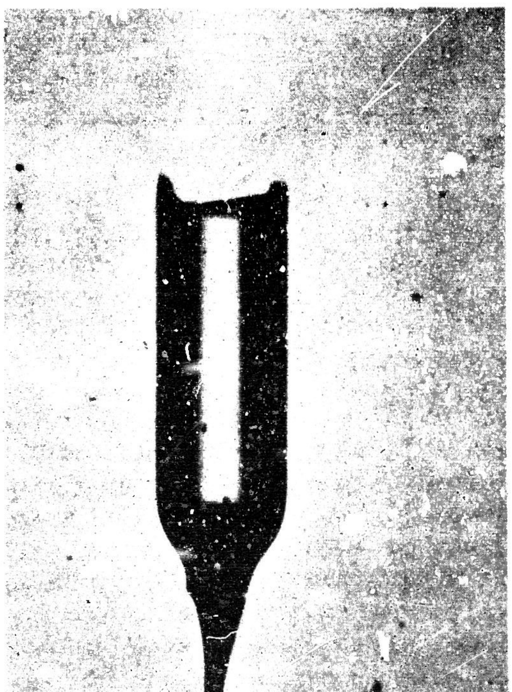
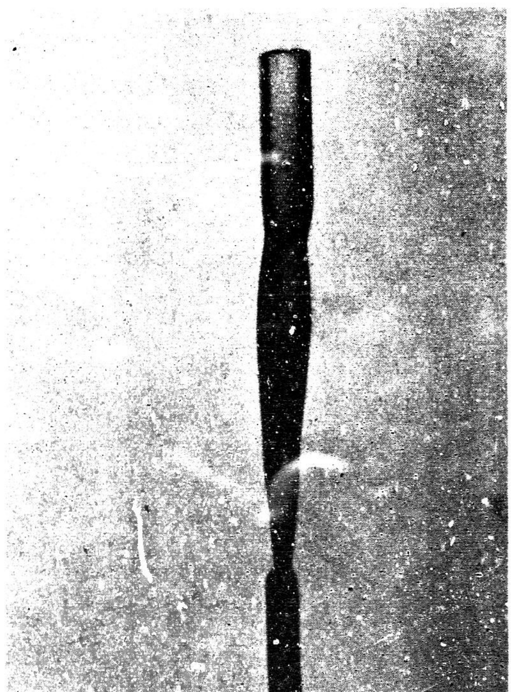


c 100X



d 35X

Figure 3

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